A continuum model for lithium plating and dendrite formation in lithium-ion batteries: Formulation and validation against experiment

Smita Sahu, Jamie M. Foster

School of Mathematics and Physics, University of Portsmouth, Lion Terrace, PO1 3HF, UK
The Faraday Institution, Quad One, Becquerel Avenue, Harwell Campus, Didcot, OX11 0RA, UK

A B S T R A C T

This work presents a novel physics-based model for lithium plating and dendrite formation in lithium-ion batteries. The formation of Li metal is an undesirable side-effect of fast charging and a primary contributor to cell degradation and failure. The model distinguishes between three types of plated Li metal, namely: (a) Li metal plated within the pores of the solid electrolyte interphase (assumed to be electronically connected to the anode and therefore recoverable); (b) dendrites protruding outside the SEI that remain electronically connected (and are therefore dangerous, potentially leading to a short circuit), and (c) electronically disconnected/“dead” Li metal outside the SEI contributing to capacity fade. The model is validated against two independent experiments. First, measurements of: (i) the cell voltage and current during a constant-current–constant-voltage charge and subsequent discharge, and (ii) the Li metal intensities (derived from operando NMR) which directly quantifies the time-resolved quantity of Li metal in the cell during use. Second, against voltage measurements during galvanostatic discharge at a range of C-rates and temperatures. Favourable agreement is demonstrated throughout; particularly in terms of the proportions of reversible and irreversible plating. We also demonstrate that the model reproduces the well-documented trends of being more prevalent at increased C-rate and/or decreased temperature.

1. Introduction

Lithium-ion batteries (LIBs) are expected to be a key technology in the low-carbon economy and although they are already commercially successful, there is appetite for improvements in cell capacity, recharging rates and device lifetime. Fast charging is desirable in order for electric vehicles to compete with the refuel times of the traditional combustion engine, but rapid charge tends to exacerbate degradation leading to shorter lifetime. Degradation comes in many forms and its study is a large field of active research; we point interested readers to several recent reviews on the area [1–6]. This study shall focus on degradation via Li plating which is known to be prevalent at high rates (as well as low temperatures and high state of charge (SOCs) [7–12]) and is a key hurdle to overcome in realising fast charging LIBs.

By far the most common anodic active material used is carbon in the form of graphite (LiC₆). It is highly conductive with a theoretical capacity of 372 mAh/g and economic [13]. Li is known to “plate” on its surface and the deposits/dendrites can grow with a needle-/bush-/hair-like morphology. In extreme cases, these dendrites can penetrate the separator, causing a short circuit and catastrophic explosion [14, 15]. Several studies have demonstrated that once plating/dendrite formation has occurred, some Li is recoverable (reversible) whilst the remainder is permanently dead (irreversible). When a significant degree of plating takes place, the Li can extend from the surface of the graphite, through the SEI, and into the electrolyte where it quickly forms a surface film (similar, yet different, to SEI and often termed lithium electrolyte interphase) [9,16,17]. Plated Li in proximity to the surface of the anode particle is typically recovered (oxidised) first [18, 19] because it is electronically connected and can therefore receive the requisite electrons [20] to undergo the reactions that allow it to be recovered. When this happens, however, the Li that is remote from the graphite’s surface is then isolated from the anode and is therefore prone to becoming “dead” (electronically disconnected) [21,22].

Previous authors have formulated physics-based models of Li plating. The first to do so was Arora et al. [23] who modelled plating using a (reversible) Butler–Volmer (BV) reaction rate. One criticism of this model is that it can predict unphysical negative amounts of Li plating. This is because their de-plating rate does not go to zero when there is no Li metal left to oxidise. Moreover, it fails to capture the formation of dead lithium, i.e., all the Li that is plated is always available for recovery. Another study, by Sikha et al. [24], formulated...
a model containing a generic side reaction, as well as a description of how the reaction product occupies an appreciable volume, thereby leading to pore clogging and hindering the ionic transport through the electrolyte. They assumed that reaction kinetics are “highly irreversible” (modelled by an ad-hoc Tafel rate) such that, if we were to consider this side reaction to represent Li plating, then oxidation is precluded. Yang et al.’s [25] model combines the mechanisms described in both Arora et al. [23] and in Singh et al. [24]; they included both SEI formation (which can lead to pore-clogging) and Li plating. However, again, they used the Tafel approximation (for both reactions) so that Li recovery is impossible. A more recent paper by the same group [26] describes reversible Li plating (using the BV rate, rather than Tafel). However, like the original work of Arora et al. [23] the model does not discern between Li metal that is recoverable vs. that which is irrecoverable. A more subtle, but important, criticism of all of the modelling work mentioned thus far is that lithium transport inside the graphite is assumed to be described by Fickian diffusion. As was shown by O’Kane et al. [27], having an accurate description of the Li transport inside the graphite is crucial to accurately capturing plating because reaction kinetics on the surface are strongly depend upon the local Li concentrations, and these are strongly affected by the transport model. O’Kane et al. [27] added non-linear transport inside the graphite to Yang’s model [26] and demonstrated its importance as well as those of temperature variations. Recent work by Ren et al. [28] made the first attempt to distinguish reversibly and irreversibly plated Li metal by modifying Arora et al.’s [23] model. Ren et al. assumed that three side reactions take place (reversible and irreversible Li plating as well as SEI formation) and that these all occur simultaneously and in direct proportion to one another; i.e., SEI formation necessarily entails Li plating and vice versa. This has the advantage of simplifying the model equations, but it contradicts various experimental observations. For example, Sun et al. [29], have demonstrated via experiment that under suitable cycling conditions, SEI thickens but no Li metal is formed. Moreover, Fang et al. [30] have used NMR spectroscopy to directly quantify the amounts of Li that is plated and that which is bound up in the SEI and have shown that two process are not linearly dependent upon one another. A body of other theoretical work [31–36] supports this conclusion that SEI formation and Li plating are independent processes. Recent work by O’Kane et al. [37] models Li plating alongside four other degradation mechanisms, however, the basis on which the Li becomes dead is not well-justified (it is assumed to follow a simple first order reaction). Moreover, it is incapable of describing the onset of lithium plating (i.e., forming Li metal when no plated Li is already present) because the reaction rate is identically zero when the concentration of Li metal is zero. Finally, we note that review by Reniers et al. [4] which gives a detailed discussion on several degradation mechanisms, coupling them together within the framework of the single particle model (SPM). The Tafel approximation is used to model the Li plating rate and therefore there is no prediction of Li de-plating. Like Reniers et al. [4] we also adopt the SPM framework as a vehicle for presenting our Li plating model. We do so in the interests of simplicity, but fully acknowledge that the end goal should be to embed any degradation model within the more realistic Doyle–Fuller–Newman (DFN) model [38–40]. To this end, in the supplementary information (SI) §2, we state the DFN model augmented with our description of Li plating, but defer solution to future work.

The overall goals of the present study are to: (i) to develop a physics-based model that remedies the shortcomings of prior work mentioned in the previous paragraph, and (ii) to provide direct validation of this model against two independent experiments. One of these experiments includes time-resolved NMR data [41], with sufficiently fidelity to capture dynamic processes under high charging rates; to the best of our knowledge this is the first time a Li plating model has been validated against such data. This type of measurement is particularly powerful for validation because it directly quantifies the amount of plated Li in-operando and is therefore a stringent test of the model’s predictive capability. Our model shall (a) distinguish three species of Li metal, namely Li metal within the pores of the SEI; Li metal dendrites outside the SEI that are electronically connected to the anode and therefore potentially dangerous sources of short-circuiting, and; Li metal outside the SEI that has become electronically disconnected and that is therefore inert/dead. It will (b) include an experimentally-informed description of the disconnection of the plated Li (becoming dead). It will (c) allow Li to plate from nucleation sites (rather than requiring that some metallic Li is already present), and (d) will not allow lithium recovery when no Li metal is present. All reaction rates are (e) taken to be described by the full BV equation (no ad-hoc Tafel approximations are used), and (f) the transfer of Li directly between the plated state and the graphite is allowed. All of this is coupled with (g) non-linear transport in the graphite and (h) the effects of temperature variations are captured.

The remainder of this paper is organised as follows: In Section 2 we formulate the model, discuss its structure and outline the method of furnishing solutions; in Section 3 we validate the model against experiment; in Section 4 we discuss the results before drawing our conclusions in Section 5.

2. Model formulation

In this study, we shall incorporate our model for Li plating into a SPM. However, there are no significant hurdles in embedding the equations governing the plating in a more complex setting, e.g., in the DFN model. Moving to the DFN setting is likely to be required before the model presented here can be used to make truly accurate predictions on realistic battery behaviour, particularly at moderate or high C-rates. To this end, the statement of the DFN model augmented with our description of plating is given in the SI §2. The SPM approach is a simplified version of the DFN in which the dynamics are assumed to be approximately uniform throughout each electrode thickness [42–45]; as such the model collapses to that of a transport problem (non-linear diffusion equation) inside a single “representative” particle in each electrode. These are coupled together by boundary conditions, and in the case of our SPM, which includes Li plating, the transport problems are also coupled via ordinary differential equations (ODEs) describing the plating rates. The cell voltage is determined by an algebraic equation. Li is transferred between the two electrodes via the electrolyte, but the electrolytic transport is not explicitly modelled, except via its presence in the cell voltage (where it appears in a linearised form, see [29]). We make the choice of using the SPM for two reasons: (i) the main aim of this study is to develop the equations governing the plating and this is best done without being encumbered by the significantly more complex partial differential equations (PDEs) in the DFN, and; (ii) the data that we shall use for model validation is purely time-dependent, and hence the spatial resolution provided by the DFN is not required.

We expand the SPM by adding three additional states (over and above the usual two, namely the anode and cathode) in which Li can reside; these are (a) Li that is plated within the SEI that remains electronically connected and hence is available for recovery, (b) Li metal in the form of dendrites outside the SEI, electronically connected to the anode and hence both recoverable and dangerous, and (c) Li metal outside the SEI that has become electronically disconnected and that is therefore irrecoverable/dead. A summary of these states and the reactions pathways is given in Fig. 1. We shall now formulate the equations governing Li transport in the anode (including the plating processes), we then do the same in cathode, and finally, we shall explain how to compute the cell voltage thereby closing the model.
3. Spherical symmetry requires Li-ion diffusivity in the anode particles (see Fig. 3(a)).

\[ \frac{\partial c}{\partial \rho} \]

is the particle radius, where \( r \) is modelled by a non-linear diffusion equation

\[ \frac{\partial D(\rho, \lambda)}{\partial \rho} = \frac{1}{r} \frac{\partial}{\partial \rho} \left( r^2 P_0(\rho, \lambda) \frac{\partial c}{\partial \rho} \right) \quad \text{for} \quad r, \rho \in [0, R_a]. \]  

(2)

where \( r_a \) is the distance from the centre of the anode particle and \( R_a \) is the particle radius, \( c_a \) is the Li-ion concentration and \( D_a(\rho, \lambda) \) is the Li-ion diffusivity in the anode particles (see Fig. 3(a)).

The diffusion coefficient shall be taken to have an Arrhenius dependence on the temperature, see the SI §3. Spherical symmetry requires

\[ -D_a(\rho, \lambda) \frac{\partial c}{\partial \rho} \bigg|_{\rho=0} = 0. \]  

3. Several reactions are possible on the surface of the anode particle as shown in Fig. 2. The outward flux of Li on the surface of the graphite is given by

\[ -D_a(\rho, \lambda) \frac{\partial c}{\partial \rho} \bigg|_{\rho=R_a} = \xi_p \frac{\rho}{F} - \xi_e c_a \]  

where \( F \) is Faraday’s constant. The quantity \( \frac{\rho}{F} \) is the current density carried by Li metal being oxidised into its positive and negative parts by introducing \( j \) into its positive and negative parts by introducing

\[ j = \frac{\xi_p}{F} \]  

and hence the initial condition is given by

\[ c_a \bigg|_{t=0} = c_{a,\text{init}}. \]  

where \( c_{a,\text{init}} \) is the constant initial Li concentration in the anode particle.

Lithium plating. The total number of mols of Li plated, \( C_{\text{tot}} \), is given by

\[ \frac{dC_{\text{tot}}}{dt} = -4\pi R_a^2 m_p \frac{\xi_p}{F} \xi_e \frac{j_{\text{pe}}}{F} A_{\text{PE}} A_{\text{PE}}^+ - \frac{N_e}{F} \left( \frac{\xi_p}{F} H(\xi_p) + j_{\text{pe}} \right). \]  

where \( j_{\text{pe}} \) is the current density carried by Li metal being oxidised into the electrolyte (\( Li_{\text{p}} = Li_{\text{p}}^+ + e^- \)), and we assume that initially there is no Li metal present. For reasons that shall become clear shortly it is useful to split \( j_{\text{pe}} \) into its positive and negative parts by introducing

\[ j_{\text{pe}}^+ = \frac{1}{2} (j_{\text{pe}} + j_{\text{pe}}) \]  

such that \( j_{\text{pe}} = j_{\text{pe}}^+ + j_{\text{pe}}^- \). We rationalise the terms on the right-hand side (RHS) of (6) as follows. The first term, \( -4\pi R_a^2 m_p \xi_p \xi_e \), accounts for the transfer of Li to/from the anode particle from/to the plated
state. The quantity \( n_{\text{pl}} \) is the molar flux of plated Li into the anode particle, and the surface area available for this flux to pass through is surface area of the particle (\( 4\pi R^3 \)) multiplied by the area fraction (equivalent to volume fraction) of plated lithium on the surface of the particle. We note that because this term contains a factor of \( \xi_p \) it naturally decays to zero when there is no lithium to recover, thus it cannot cause unphysical negative amounts Li metal. The second and third terms account for the formation/oxidisation of plated Li directly out of/into the electrolyte. The second term accounts for this process occurring throughout the thickness of the SEI whilst the third accounts for it via nucleation sites on the surface of the graphite. The quantity \( A_{\text{pe}} \) is the total surface of the pores in the SEI, see Fig. 2, and therefore \( A_{\text{pe}} \xi_p \) is the total area between plated Li and electrolyte through the SEI. Thus, the second term, \(-j_{\text{pe}} A_{\text{pe}} \xi_p / F\) is the rate of formation of Li metal throughout the SEI. Just like the first term of the RHS of (6), the second term also decays to zero when \( \xi_p \rightarrow 0 \) meaning that oxidation cannot occur when there is no Li metal. The quantity \( \Gamma \) is the area of the graphite's surface where nucleation can occur. Thus multiplying \( \Gamma \) by \(-j_{\text{pe}} / F\) gives the total rate of transfer of Li into the plate from the electrolyte. Since the area through which this transfer is fixed (unlike the previous two terms it does not contain a factor of \( \xi_p \)), in order to prevent negative Li metal concentrations, we need to ensure that this rate is suppressed when there is no Li metal to oxidise and when \( j_{\text{pe}} \) is positive (the local electrochemistry is such that oxidation is favourable). We do so by splitting \( j_{\text{pe}} \) into its positive and negative parts, using (8), and multiplying the positive part, \( j_{\text{pe}}^+ \), by \( H(\xi_p) \); Heaviside step function with \( H(0) = 0 \). Thus, consistent with the experimental literature \( [18,47,49,50] \), plating must be initiated on nucleation sites.

We now need to segregate the total amount of metallic Li, \( C_{\text{out}} \), into that which resides within the pores of the SEI (\( C_{\text{in}} \)), and that which extends outside the film (\( C_{\text{out}} \)) such that

\[
C_{\text{tot}} = C_{\text{in}} + C_{\text{out}}.
\]

As previous authors have suggested \( [9,16,17,20] \) we shall assume that the Li metal remains recoverable whilst it resides sufficiently close enough to the graphite's surface (i.e., within the SEI). Moreover, we shall assume that Li metal grows within the pores of the SEI until those pores are sufficiently full (that is until the volume fraction of Li metal in the pores, \( \xi_p \), reaches \( \xi^* \)), at which point any further growth will extend outside of the SEI. Thus

\[
\frac{dC_{\text{in}}}{dt} = \begin{cases} 
\frac{dC_{\text{tot}}}{dt} & \text{if } 0 < \xi_p < \xi^* \text{ or } \frac{dC_{\text{out}}}{dt} \leq 0, \\
0 & \text{otherwise}, 
\end{cases}
\]

\[
\frac{dC_{\text{out}}}{dt} = \begin{cases} 
\frac{dC_{\text{tot}}}{dt} & \text{if } 0 < \xi_p < \xi^* \text{ or } \frac{dC_{\text{out}}}{dt} \leq 0, \\
0 & \text{otherwise}. 
\end{cases}
\]

Eqs. (10)–(11) ensure that the amount of Li outside of the pores cannot reduce with time encapsulating the assumption that Li extending outside the SEI is irrecoverable (although not necessarily electronically disconnected). We equip the following initial conditions

\[
C_{\text{in}}|_{t=0} = 0, \quad C_{\text{out}}|_{t=0} = 0.
\]

Summing (10) and (11), integrating with respect to time and imposing (7) and (12) recovers (9), as it should. The volume fraction of the surface film occupied by Li metal and the number of mols of recoverable Li metal are related via

\[
c_{\text{in}} = \frac{4\pi R^3 (\xi^* - R_s^3)}{3V_L},
\]

where \( \xi_s - R_s \) is the SEI thickness and \( V_L \) is the partial molar volume of Li metal.

**Distinguishing dead Li and electronically connected (dangerous) dendrites.**

When considering battery safety it is of paramount importance to be able to discern when dendrites are inert and when they are live and a potential source of short-circuiting. Li metal outside of the porous SEI is apportioned into two phases; \( C_{\text{out}} \) denotes Li metal outside the SEI that remains electronically connected to the anode whilst \( C_{\text{out}} \) denotes Li metal outside the SEI that is electronically disconnected and therefore inert/dead. We have

\[
C_{\text{out}} = C_{\text{out}}^+ + C_{\text{out}}^-
\]

We assume that as Li metal grows outside of the SEI it does so in the form of dangerous live dendrites. These electronically connected dendrites become severed from the anode if, at a later time, all of the Li metal within the porous SEI has been oxidised such that there is no longer an electronically conducting medium bridging the SEI film and connecting the dendrites to the graphite. Hence

\[
C_{\text{out}}|_{t=0} = 0 \quad \text{when } \xi_p = 0,
\]

\[
\frac{dC_{\text{out}}^+}{dt} = \frac{dC_{\text{out}}^-}{dt} \quad \text{otherwise}.
\]

**Charge conservation in the anode.** Charge conservation in the negative electrode requires

\[
\xi_s 4\pi R^2 j_{\text{ae}} + j_{\text{pe}} A_{\text{pe}} \xi_p + \Gamma H(\xi_p) \frac{(i(t) - j_{\text{pe}})}{n_a} = 0.
\]

Here, \( n_a \) is the total number of particles in the anode which is given by \( n_a = Al_{\text{AE}} A_{\text{pe}} / (4\pi R^3 / 3) \) where \( A \) and \( L_a \) are the cross-section area and the thickness of the negative electrode and \( c_a \) is the volume fraction of graphite in the anode. The total current applied to the cell, \( I(t) \), is defined such that \( I(t) < 0 \) corresponds to charge and \( I(t) > 0 \) to discharge. The relationship (16) ensures that there is sufficient (de)intercalation and (de)plating to sate the current demand.

**Reaction between the anode particle and the electrolyte.** The (de)intercalation reaction is given by the following BV equation

\[
j_{\text{ae}} = 2Fk_{\text{ae}} \sqrt{c_a l_{\text{pe}} R_s} \left( c_{a_{\text{max}} - c_a l_{\text{pe}} R_s} \right) \sinh \left( \frac{\eta_{\text{ae}}}{2RT} \right),
\]

where \( \eta_{\text{ae}} \) is termed the surface overpotential (it is the difference between electrochemical potentials between a Li-ion in the anode and that in the electrolyte) and is given by

\[
\eta_{\text{ae}} = \Psi_a - U_{\text{eq}}(c_a l_{\text{pe}} R_s).
\]

Here \( \Psi_a \) is the electric potential difference between anode and electrolyte, \( U_{\text{eq}} \) is the equilibrium potential, \( c_{a_{\text{max}}} \) is the maximum concentration of Li in the anode particle, \( R_s \) is the radius of the anode particle, and \( c_a \) is the (constant) Li-ion concentration in the electrolyte and \( k_{\text{ae}} \) is a reaction rate constant. Note that we have assumed a ‘symmetric’ form of BV (the transfer coefficients \( a_a = a_e = 0.5 \)) but it is straightforward to generalise if needed.

**Reactions between the plated Li and the electrolyte.** The current density due to the oxidation of Li metal directly into the electrolyte, \( j_{\text{pe}} \), is given by

\[
j_{\text{pe}} = 2Fk_{\text{pe}} \sqrt{c_a l_{\text{pe}} R_s} \sinh \left( \frac{\eta_{\text{pe}}}{2RT} \right),
\]

where \( \eta_{\text{pe}} \) is the overpotential between Li plating and electrolyte and given by

\[
\eta_{\text{pe}} = \Psi_a - \Delta.
\]
here $k_{pa}$ is the reaction rate constant between the anode particle to the electrolyte, $V_{Li}$ is the partial molar volume of Li metal, and $\Delta$ is the overpotential required for Li plating. We shall follow and set $\Delta = 0$ [26,27,37] but note that there is mounting evidence to suggest that $\Delta$ should have a small negative value of around $\Delta = -1.39$ eV [51] depending on the details of the surface chemistry of the graphite [46]. In contrast to (17) the exchange current density (prefactor of the hyperbolic sine) in (19) is only dependent upon the Li-ion concentration in the electrolyte; this is because the concentration of Li in Li metal is constant (unlike the concentration of Li in graphite).

Reactions between the plate Li and the anode particles. The molar flux of Li from the plated Li to the anode particle, $m_{pa}$, is given by

$$m_{pa} = 2k_{pa} \left( \frac{c_{max} - c_e|_{r=R_e}}{V_{Li}} \right) \sinh \left( \frac{F \eta_{pa}}{2RT} \right),$$  

(21)

where $\eta_{pa}$ is the overpotential between plating to the anode particles given by

$$\eta_{pa} = U_{eq,a} - \eta_e - \Delta,$$

(22)

where $k_{pa}$ is reaction rate constant.

2.2. The cathode

The Li transport within the cathode particles is modelled by the following non-linear diffusion equation, and boundary and initial conditions

$$\frac{\partial c_e}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_e(c_e,T) \frac{\partial c_e}{\partial r} \right)$$

for $r_e \in [0, R_e]$.

$$-D_e(c_e,T) \frac{\partial c_e}{\partial r} \bigg|_{r_e=R_e} = \frac{j_{ce}}{F},$$

(23)

where $r_e$ is the distance from the centre of the cathode particle, $c_e$ is the Li-ion concentration in the cathode particle, $D_e(c_e,T)$ is the Li-ion diffusivity in the cathode particles, with Arrhenius temperature dependence (see Fig. 3(b)). The boundary condition follows from spherical symmetry whilst the latter specifies the outward Li-ion flux in terms of the surface (de)intercalation current density, $j_{ce}$. The initial Li concentration in the cathode is given by $c_e|_{t=0} = c_e|_{init}$.

The current density from the cathode particle to the electrolyte is given by the following symmetric BV rate

$$j_{ce} = 2 F k_{ce} \sqrt{c_e c_e|_{r=R_e}(c_{max} - c_e|_{r=R_e})} \sinh \left( \frac{F \eta_e}{2RT} \right),$$

(24)

where $\eta_e = \Psi_e - U_{e,eq}(c_e|_{r=R_e})$.

here, $\eta_e$ is the surface overpotential, $\Psi_e$ is electric potential difference between cathode and electrolyte, $c_{max}$ is the maximum Li concentration in the cathode particles, $c_e$ is the constant Li ion concentration in the electrolyte, and $k_{ce}$ reaction rate constant for cathode to electrolyte. The total number of particles in the cathode $n_e$ (given by $A L_e/\pi R_e^2$) where $A$ is the cross sectional area of the cathode, $L_e$ thickness and $\phi_e$ the volume fraction of active material in the cathode.

Charge conservation in the cathode yields

$$4 \pi R_e^2 j_{ce} = -\frac{I(t)}{n_e},$$

(25)

thereby ensuring that the (de)intercalation reaction in the cathode is sufficient to meet the current demand.

2.3. The cell voltage

The cell voltage is defined as

$$V = \Phi_a - \Phi_e,$$

(26)

where $\Phi_a$ and $\Phi_e$ are the potentials of the active materials in the anode and cathode respectively. Consistent with the premise of the SPM model, we assume that the solid matrix in both electrodes have sufficiently low resistances that, to a good approximation, no voltage is dropped via electron conduction and hence the both these potentials are uniform in space. The quantities $\Phi_a$ and $\Phi_e$ can be expressed as

$$\Psi_a = \Phi_a - \Phi_{ae}, \quad \Psi_e = \Phi_e - \Phi_{ae},$$

(27)

where $\Phi_{ae}$ and $\Phi_{ae}$ are the potentials in the electrolyte (as measured by a Li reference electrode) immediately outside the representative anode and cathode particle respectively. Substituting these relationships into (26), and eliminating $\Psi_a$ and $\Psi_e$ using (18) and (24) yields

$$V = (U_{eq,c} + \eta_e) - (U_{eq,a} + \eta_a) + (\Phi_{ae} - \Phi_{ae}).$$

(28)

The quantity in the first (second) set of parenthesis on the RHS can be identified as the potential drop between the representative cathode (anode) particle and the adjacent electrolyte. The quantity in the third set of parenthesis is the voltage dropped via ionic conduction in the electrolyte. This drop can be modelling in a number of different ways. Here we opt to take a simple approach and assume that the drop across the electrolyte is Ohmic. As such we can write

$$V = (U_{eq,c} + \eta_e) - (U_{eq,a} + \eta_a) - IR_e,$$

(29)

where $R_e$ is the resistance of the electrolyte. We approximate this quantity in a manner consistent with the SPM, namely by setting $c_e$ = constant in the MacInnes equation (see equation (4.15c) in Richardson et al. [52]), by $R_e = L_e/\kappa AB$, where $L_e$ is the distance between the representative anode and cathode particles, $\kappa$ the conductivity of the electrolyte, $B$ the permeability and $A$ is the electrode cross-sectional area.

2.4. Summary of the model structure and numerical solution

Eqs. (1)–(25) along with (29) comprises a closed system of equations to solve for the cell voltage, $V(t)$, given an input current, $I(t)$. It is worth noting that the solution can be furnished in a series of de-coupled steps whereby we can solve the equations in the anode and cathode separately, and then in third and final step we compute the cell voltage. In the anode we need to determine 17 quantities, namely $c_e, C_{tot}, C_{out}, C_{out}, \xi_{eq}, c_{eq}, c_{eq}, \xi_{eq}, j_{eq}, j_{eq}, j_{eq}, \eta_{eq}, \eta_{eq}, \eta_{eq}, \eta_{eq}$ and $\Psi_e$ and the equations formulated in Section 2.1 are a closed system to be solved for them. In the cathode we need to determine 4 quantities: $c_e, j_{eq}, \eta_e$ and $\Psi_e$. A closed system to determine these has been formulated in Section 2.2. In the final stage we can use quantities determined in solving the equations in the anode an cathode in (29) which gives the cell voltage. We note that this structure, is common to many SPM-type models [42,43,45].

The model must be solved numerically. We use the method of lines in which spatial derivatives are discretised using the finite element method and time integration is achieved using MATLAB’s ode15s. Details of the numerical scheme and its validation against analytical conservation properties are given in the SI §1.

3. Validation against experiment

In this section we validate our model against two independent experiments. First, we leverage the data in Sanders et al. [41] who measure the cell voltage, and simultaneously collect NMR data (allowing them to directly quantify the amount of Li metal present) during constant current constant voltage (CCCV) charge, a short rest at open circuit, and subsequent constant current (CC) discharge of a graphite/NMC622 cell. We shall briefly outline the experimental protocol but refer readers to Sander et al. [41] for full detail. Second, we fit our model to the data in Ge et al. [53] who have measured the voltage of a graphite and LNC (Li$_x$Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$) cell during a series of galvanostatic discharges at varying C-rate and temperature. The details of this second validation are presented in the SI §5.
A graphite (4.4 mAh cm\(^{-2}\)) anode and LiNi\(_{0.6}\)Mn\(_{0.2}\)Co\(_{0.2}\)O\(_2\) (NMC622, 4.5 mAh cm\(^{-2}\)) cathode were harvested from an unused commercial EV battery and rehoused in a bespoke body. We focus on the data obtained during the second cycle, thereby avoiding the well-documented quirks associated with the rapid SEI growth during the formation cycle [8,36,37].

The cell was charged at 1C (0.0229 A) until the voltage reached 4.25 V. It was then held at this voltage until the current dropped to a value corresponding to C/4 then the cell was rested at open circuit for 30 min, whereafter it was discharged at C/5 until voltage drop to 2.5 V. The resulting voltage and current is shown in Fig. 4.

The key novelty in Sanders et al. [41], and the reason that this particular data set serves as an excellent model validation, is an improved experimental design which allows the collection of NMR data with sufficiently high time resolution to capture dynamic processes under high rates. One-pulse NMR spectra were collected every 3 min, see Fig. 5, giving a well-resolved picture of amount of Li metal present in the cell. As far as the authors are aware, what we present below is the first validation of a model against experimentally measured real-time Li metal concentrations, a much more direct validation than the typical comparison with voltage curves or differential voltage analyses seen elsewhere in the literature.

### 3.1. Summary of the experimental data in Sanders et al. [41]

A graphite (4.4 mAh cm\(^{-2}\)) anode and LiNi\(_{0.6}\)Mn\(_{0.2}\)Co\(_{0.2}\)O\(_2\) (NMC622, 4.5 mAh cm\(^{-2}\)) cathode were harvested from an unused commercial EV battery and rehoused in a bespoke body. We focus on the data obtained during the second cycle, thereby avoiding the well-documented quirks associated with the rapid SEI growth during the formation cycle [8,36,37].

The cell was charged at 1C (0.0229 A) until the voltage reached 4.25 V. It was then held at this voltage until the current dropped to a value corresponding to C/4 then the cell was rested at open circuit for 30 min, whereafter it was discharged at C/5 until voltage drop to 2.5 V. The resulting voltage and current is shown in Fig. 4.

The key novelty in Sanders et al. [41], and the reason that this particular data set serves as an excellent model validation, is an improved experimental design which allows the collection of NMR data with sufficiently high time resolution to capture dynamic processes under high rates. One-pulse NMR spectra were collected every 3 min, see Fig. 5, giving a well-resolved picture of amount of Li metal present in the cell. As far as the authors are aware, what we present below is the first validation of a model against experimentally measured real-time Li metal concentrations, a much more direct validation than the typical comparison with voltage curves or differential voltage analyses seen elsewhere in the literature.

### 3.2. Model fit

On adjusting the parameters marked with a † in Table 1 we obtain the fits shown in Figs. 4 and 5. In general the agreement between model and experiment is very favourable in terms of cell voltage and current, as well as the amounts of Li metal. A detailed interpretation of the results is the topic of the subsequent section, however, it is pertinent to rationalise the discrepancies between model and data here.

Fig. 4(c) reveals that the model has a tendency to slightly (by <5.7%) under-predict the cell voltage; consequently the initial charge time is also under-estimated. With reasonable confidence we speculate that this difference can be ascribed to our choice to employ the SPM model rather than the full DFN model. In doing so, we have neglected inhomogeneities in both the electrode parameters and in the states (Li concentrations and potentials) across the cell. It is well-documented that at rates of 1–2C and for cells containing graphite anodes the discrepancy between the DFN and SPM (with identical parameterisation) is in the range of 2%–5% (see, e.g., Fig 4 in [45], Fig 9 in [63], Fig. 4 in [44] and Fig. 2 [43]). For C-rates lower than 1C the agreement between the SPM and DFN is typically negligible, and at C-rates higher than 2C the disagreement is typically significant. Moreover, we have made the common approximation that all particles in each electrode have the same size; however, some variation almost certainly exists in reality. As has been shown in Fig. 5 of Kirk et al. [64] and Fig. 4 of Kirk et al. [65] accounting for these variations can affect cell voltage predictions by a few percent, in line with the size of discrepancies we
Table 1
List of model parameters. We note that throughout the model, the parameters \( k_{ps} \) and \( A_p \) only ever appear as a product and therefore they should be counted as a single fitting parameter rather than two.

<table>
<thead>
<tr>
<th>Param./Ftn.</th>
<th>Description</th>
<th>Anode</th>
<th>Cathode</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{el} )</td>
<td>Electrode particle radius (^a)</td>
<td>9</td>
<td>9</td>
<td>( \mu m )</td>
</tr>
<tr>
<td>( t_{el} )</td>
<td>Electrode thickness (^a)</td>
<td>50</td>
<td>50</td>
<td>( \mu m )</td>
</tr>
<tr>
<td>( A )</td>
<td>Electrode cross-section area (^a)</td>
<td>( 5.51 \times 10^{-4} )</td>
<td>( 5.51 \times 10^{-4} )</td>
<td>( m^2 )</td>
</tr>
<tr>
<td>( c_{el} )</td>
<td>Volume fraction of electrode (^b) area particles in each electrode</td>
<td>0.9497</td>
<td>0.8235</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( n_{el} )</td>
<td>Number of particles in electrode (^c)</td>
<td>( 8.5682 \times 10^8 )</td>
<td>( 7.4297 \times 10^8 )</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( c_{el}^{max} )</td>
<td>Maximum Li concentration in the cathode particle (^d)</td>
<td>–</td>
<td>42,000</td>
<td>mol m(^{-3})</td>
</tr>
<tr>
<td>( c_{el}^{max} )</td>
<td>Maximum Li concentration in the anode particle (^{[54,55]})</td>
<td>32,800</td>
<td>–</td>
<td>mol m(^{-3})</td>
</tr>
<tr>
<td>( c_{el, int} )</td>
<td>Initial Li concentration in the electrode particle (^e)</td>
<td>2008</td>
<td>37,800</td>
<td>mol m(^{-3})</td>
</tr>
<tr>
<td>( c_{e} )</td>
<td>Li concentration in electrolyte (^{[54,55]})</td>
<td>1000</td>
<td>1000</td>
<td>mol m(^{-3})</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>SEI thickness on anode (^f)</td>
<td>100</td>
<td>–</td>
<td>nm</td>
</tr>
<tr>
<td>( D_{Li}(c_{el}, T) )</td>
<td>Li diffusion coefficient in the electrode particle (^{[54,59,60]})</td>
<td>–</td>
<td>–</td>
<td>( m^2 s^{-1} )</td>
</tr>
<tr>
<td>( \nu_{Li} )</td>
<td>Partial molar volume of Li metal (^{[25]})</td>
<td>( 1.297 \times 10^{-5} )</td>
<td>–</td>
<td>( m^3 mol^{-1} )</td>
</tr>
<tr>
<td>( \beta(x) )</td>
<td>Permeability factor in electrode matrix (^{[54,55]})</td>
<td>0.162</td>
<td>0.153</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>Electrolyte conductivity (^{[54,55,59]})</td>
<td>1</td>
<td>1</td>
<td>A m(^{-1} V^{-1})</td>
</tr>
<tr>
<td>( F_{e, t} )</td>
<td>Activation energy for diffusion (^b) coefficients (^{[54,55]})</td>
<td>30,300</td>
<td>80,600</td>
<td>J mol(^{-1})</td>
</tr>
<tr>
<td>( P_{e, t} )</td>
<td>Activation energy for reaction rate constants (^{[54,55]})</td>
<td>43,600</td>
<td>53,400</td>
<td>J mol(^{-1})</td>
</tr>
<tr>
<td>( F )</td>
<td>Faraday's constant (^{[61]})</td>
<td>96,485</td>
<td>96,485</td>
<td>A s mol(^{-1})</td>
</tr>
<tr>
<td>( R )</td>
<td>Universal gas constant (^{[61]})</td>
<td>8.3145</td>
<td>8.3145</td>
<td>J K(^{-1}) mol(^{-1})</td>
</tr>
<tr>
<td>( \xi )</td>
<td>Volume fraction of SEI in surface film (^{[58,62]})</td>
<td>0.81</td>
<td>–</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( \xi_{Li}^{ini} )</td>
<td>Initial volume fraction of Li plating in surface film (^{[25,37]})</td>
<td>0</td>
<td>–</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( \xi_{PS, int} )</td>
<td>Volume fraction of Li plating available for Li plating in a surface film (^{[58,62]})</td>
<td>0.085</td>
<td>–</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( k_{e, t, e, o, 0} )</td>
<td>Reaction rate constants at 22.85 °C electrode to electrolyte (^{[25,37]})</td>
<td>( 5.196 \times 10^{-10} )</td>
<td>( 1.995 \times 10^{-9} )</td>
<td>m(^{1/2}) mol(^{-1/2}) s(^{-1})</td>
</tr>
<tr>
<td>( k_{pe} )</td>
<td>Reaction rate constant (^{[54]}) plated Li to electrolyte</td>
<td>( 1 \times 10^{-9} )</td>
<td>–</td>
<td>m(^{1/2}) mol(^{-1/2}) s(^{-1})</td>
</tr>
<tr>
<td>( k_{ps} )</td>
<td>Reaction rate constant (^{[54]}) plated Li to anode</td>
<td>0</td>
<td>–</td>
<td>m(^{1/2}) mol(^{-1/2}) s(^{-1})</td>
</tr>
<tr>
<td>( N )</td>
<td>Area of anode particle available for nucleation (^{[61]})</td>
<td>( 2.1 \times 10^{-10} )</td>
<td>–</td>
<td>( m^2 )</td>
</tr>
<tr>
<td>( A_p )</td>
<td>Surface area of the pores in the SEI (^{[61]})</td>
<td>1.02 \times 10^{-9}</td>
<td>–</td>
<td>m(^2)</td>
</tr>
<tr>
<td>( U_{eq, t} )</td>
<td>Equilibrium potential of electrode particles (^{[25,37]})</td>
<td>Fig. 3(c)</td>
<td>Fig. 3(d)</td>
<td>V</td>
</tr>
</tbody>
</table>

\(^a\)Measured by Sanders et al. \(^{[41]}\).
\(^b\)Provided by the manufacturer.
\(^c\)Fitted.
\(^d\)Taken from literature.

see here. Thus, the small discrepancies between model and experiment are likely not a failing of our plating model and may well be remedied by applying our plating model in the full DFN and/or by accounting for a particle size distribution. An excellent example of the DFN’s ability to predict experimental results can be found in Korotkin et al. \(^{[61]}\) and a recent review by Wang et al. \(^{[58]}\) discussed some of the challenges associated with fully parameterising the DFN model.

Applying our model in the context of the DFN would hamper presentation of the Li plating model itself (the main focus of the paper) and is therefore beyond the scope of the current work. Nonetheless, we fully acknowledge that utilising our plating model in the DFN model is important; in fact it is likely to be a key step en route to using our model to address practical questions of import, e.g., to help identifying better/safer charging strategies. To this end, in §2 of the SI, we state our model in the context of the full DFN, and solving this will be the topic of future work.

It is noteworthy that a good fit was obtained in a regime where the quantity \( k_{ps} = 0 \), such that transfer of Li directly between the plated state and the graphite was precluded. This suggests that Li recovery predominantly occurs via the electrolyte however, a more involved study and sensitivity analysis would be needed to confirm that the fit we have obtained is uniquely good. We anticipate that this analysis will form the basis of a future publication.
Before moving on we briefly mention a second validation against the data presented in Ge et al. [53], and reported in §5 of the SI. On adjusting only two fitting parameters we were able to obtain a very favourable agreement between our model and experimental galvanostatic discharge curves at a range of temperatures and C-rates. The data in Ge et al. is not accompanied by information on the amount of Li metal present in the cell in-operando, and so it a less convincing validation than that against Sanders et al.[41]; nevertheless it gives further credence to our model.

4. Results

First we shall give a detailed interpretation of Figs. 4 and 5, before moving on to explore the influence of temperature on Li plating.

4.1. Discussion of model fit to Sanders et al. [41]

The initial charging period. First, we focus on the black portions of the curves throughout Figs. 4 and 5, the initial charging period. We see that the current is sustained almost entirely by intercalation; $j_{\text{in}}$ is insignificant compared to $j_{\text{ae}}$, see Figs. 4(a), 4(b) and 5(d). The Li-ion concentration inside the anode particle exhibits plateaus, signatures of the phases changes, and an upshot of the highly non-linear diffusivity, see Fig. 3(a). Just prior to reaching the cut-off voltage, which triggers the end of charge, the surface of the graphite becomes saturated with Li$^+$ (this is reflected in $\Psi_{a}$ becoming negative, see Fig. 5(c)); the rate of intercalation drops markedly, being limited by diffusion inside the graphite, which is the process by which Li$^+$ moves towards the core freeing up space near the particle surface. Charge transfer is now sustained, in part, by Li-plating.

The hold at 4.2 V. Referring now to the green section of the curves, we see that the Li metal is initially plated into the pores within the SEI ($C_{\text{in}}$ increases, but $C_{\text{out}}$ does not, see Fig. 5(b)) but later (just short of 1 hr into the experiment) a sufficient amount of Li metal has been created that dendrites begin to form outside the film; see the green curve crossing the red one in Fig. 5(b) and $C_{\text{out}}$ begins increasing. It is this situation that is dangerous because the growing dendrites ($C_{\text{out}}$) remain connected to the anode via the Li metal in the pores; thus if the dendrites were to grow to such an extent that they penetrate the separator, thereby contacting the cathode, they would cause a short-circuit, potentially triggering thermal runaway and even a catastrophic explosion.

The hold at open circuit. When the current cut-off is reached, and the hold at open circuit begins (magenta curves), the overpotential in the anode, $\Psi_{a}$ (see Fig. 5(c)), becomes positive (larger than $\Delta$) and hence
Fig. 5. (a) The total amount of plated Li, $C_{\text{tot}}$, vs. time (b) $C_{\text{tot}}$ and its constituent parts; $C_{\text{in}}$, the reversibly plated Li, and $C_{\text{out}}$, the dead Li. Throughout black curves represent those during 1C charge, green during constant voltage hold at 4.25 V, magenta during the rest period and cyan curve during C/5 discharge. The red line is the threshold volume fraction available for Li-plating. (c) Potential difference between the anode (cathode) and electrolyte $\psi_a$ ($\psi_c$) vs. time. (d) Reaction rate between the anode and electrolyte $j_{ae}$ and that between Li metal and the electrolyte $j_{pe}$ vs. time. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

conditions are favourable for the oxidisation of the Li metal so that the Li metal in pores of the SEI begins to be recovered ($C_{\text{in}}$ decreases, but $C_{\text{out}}$ does not). Even though the Li metal content in the SEI film is decreasing it remains non-zero, thereby providing an pathways for electron conduction between the anode and the dendrites. As such, the device remains in a dangerous state and if the current were to be reversed, such that charging were to resume, short-circuiting is still a possibility.

The discharge period. During the final discharge period (cyan curves), we see the concentration of Li$^+$ on the surface of the graphite begin to decrease (see Fig. 4(a)). Contemporaneously, there is a slightly increase in the oxidation rate of Li within the pores until the pores fully empty of Li metal. Just after 2 h into the experiment the pores of the SEI completely empty of Li metal ($C_{\text{in}} = 0$), the electrical connection between the Li metal outside the SEI and the anode is severed so that the Li metal there becomes dead (for the first time $C_{\text{out}}^0 > 0$) and the danger of short-circuit is averted. The formation of dead Li contributes towards a loss of lithium inventory, and hence cell capacity. At the end of the CCCV cycle around 25% of the Li that was plated remains in metallic form outside of the SEI film and is permanently lost/dead, having lost its connection with the anode.

4.2. The effect of temperature variations

Having fit the experiments in [41] and interpreted the cells internal dynamics via our model, we now move on to explore the role of temperature variations. It is well-known that Li-plating occurs most dramatically during fast charging and at low-temperature [1,9,53,66]. The role of temperature variations is explored in Fig. 6. The diffusion coefficients in both anode and cathode (shown in Fig. 3), as well as the reaction rates between the electrodes and electrolyte are taken to have an Arrhenius temperature dependence with activation energies given in Table 1. Fig. 6 shows model simulations in which the cell is charged and discharged with constant current at 1C at a variety of different temperatures in the range 2°C–22°C. We observe that as the temperature decreases the propensity for Li-plating increases (see Fig. 6(d)). This trend can be ascribed, at least partially, to the decreased rates of Li transport within the graphite at low temperatures which leads to the saturation of the graphite surface at earlier times and hence Li plating.

5. Conclusion

We have developed a novel physics-based model for Li plating and presented it in the context of the single particle model. However, its generalisation for use in more complex models, e.g. the DFN, is straightforward. The statement of the DFN supplemented with our
Fig. 6. (a) The cell voltage during 1C charge–discharge cycle at different temperatures and (b) the amount of plated Li during those cycle. (c) The amount of reversible Li metal during 1C charge–discharge at different temperatures and (d) the amount of irreversible plated Li during charge–discharge cycle.

description of Li plating is given in the SI. The model has several properties, several of which are novel, and are known to be needed in order to replicate experimentally observed phenomena: The model (i) distinguishes three forms of plated Li (that within the pores of the SEI, that outside the SEI that remains electronically connected (dangerous dendrites), and that outside the SEI that it electronically inert), (ii) allows Li metal to form via nucleation sites (rather than requiring that some metallic Li is already present), (iii) ensures that oxidation cannot occur when there is no Li metal available to recover, (iv) contains full Butler–Volmer reaction rates (rather than ad-hoc Tafel approximations) and (v) allows the transfer of Li directly between the plated state and the graphite. Li metal within the SEI is available for recovery because it can receive the requisite electrons to undergo the reactions that allow it to re-enter the electrolyte/graphite). Contrastingly, the Li metal the protrudes outside the SEI cannot be recovered, and once it has had its electronic connection to the anode severed (if/when the pores in the SEI have emptied of conducting Li metal) it becomes inert/dead and therefore contributes to capacity fade. The Li metal that remains electronically live outside of the SEI represents dangerous dendrites that are potential causes of short-circuiting and cell failure.

The model has been validated against two independent experiments. First, cell voltage and current measurements during a CCCV (dis)charge protocol, accompanied with NMR measurements characterising the amount of Li metal in the cell in operando. As far as we are aware this is the first time that such a direct validation of a Li plating model has been given. Highly favourable agreement has been demonstrated particularly in terms of the amounts and rates of both reversible and irreversible Li plating. Second, against cell voltage measurements at a range of C-rates and temperatures. Again, very favourable agreement has been observed. Following validation, we demonstrated that higher C-rates and lower temperatures are conducive to Li plating and hence cell degradation.

Safely increasing the charging rate of Li-ion batteries is a key hurdle that must be overcome to help electric vehicles compete with the refuelling times of traditional combustion engines. This work paves the way for future work to use our Li plating model in the context of the more realistic full DFN model and to begin to identifying fast charging strategies that are safer and/or cause less Li plating.

The model that we have presented is, as far as we are aware, the most complete description of Li plating available in the literature. By modelling more electrochemical processes than its predecessors it is able to predict additional useful information about the internal states of a cell. However, this benefit is accompanied by an increased burden in terms of parameterisation (the model contains more parameters that must be determined before its utility can be realised). The description of plating in our model contains 6 scalar parameters (see Table 1 and/or §4 of the SI) that is up to 5 more than its simpler counterparts (e.g. 5 more than Arora et al. [23], 1 more than Ren et al. [28]), but it comes with the benefit of being able to discern between recoverable Li inside the SEI, dangerous dendrites and dead Li outside the SEI. Moreover,
it does not suffer from unphysical assumptions, e.g., about Li plating being a fundamentally irreversible process, or about interdependence between Li plating rates and other parasitic side reactions; the latter is the case for the most sophisticated model prior to this work [28]. Whether these benefits are worth the cost remains an open question, and the answer likely depends upon the aim of the modelling investigation in question. Nonetheless, in cases where it is important is disentangle different forms of plated Li (e.g. in identifying safe fast-charging protocols) we are confident that this model has a role to play.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

**Data availability**

Data will be made available on request.

**Acknowledgements**

The work of both SS and JF was supported by the Faraday Institution, UK (grant number FIRG003). The authors would like to thank Kevin Sanders and Gillian R. Goward for providing the experimental data and G. Richardson for insightful discussions.

**Appendix A. Supplementary data**

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.est.2022.106516.

**References**


